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EXECUTIVE SUMMARY

DRY DEPOSITION OF ACIDIC GASES AND PARTICLES

FINAL REPORT
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Introduction

The dry deposition of acidic gases and particles is of special concern in semi-arid California. Assessment of the possible impact of dry acid deposition on the environment requires the use of appropriate measurement methods which, however, are still under development because dry deposition is a complex process that is incompletely understood.

The present work is Phase III of a multi-year program funded by the Air Resources Board through the Kapiloff Acid Deposition Act of 1982. The objectives of the program are:

1. To study the mechanisms of dry deposition in order to provide a better basis for monitoring methods.
2. To develop measurement techniques suitable for long term monitoring of dry acid deposition.
3. To make baseline measurements of dry acid deposition at representative sites in California.

Phase I

A method which combines ambient concentrations and deposition velocities to obtain deposition fluxes was selected for the development of monitoring techniques for dry acid deposition. All of the major acidic gas and particle species were sampled by methods designed to minimize artifacts, volatilization losses and interferences. Other pollutants and meteorological parameters were monitored. Sampling was conducted at Martinez, San Jose and Democrat Springs (Kern River canyon east of Bakersfield).

The results established baseline values of ambient concentrations of acidic pollutants at these California locations and data on their diurnal variations. Redundant sampling and ion balances confirmed the quantitative accuracy of the sampling techniques.

Phase II

The baseline measurements of acidic pollutant concentrations were extended to the important Los Angeles basin. The highest acid concentrations were detected at Tanbark Flats, representative of vulnerable forested mountain areas downwind of Los Angeles. Particle size distributions were obtained for specific chemical species including hydrogen

ion, the first such data available. Over 50% of the nitrate at West Los Angeles was in the coarse fraction. This is significant since the deposition velocity increases rapidly with particle size.

Deposition velocities were measured for sulfate and nitrate depositing on leaves of two species of Ligustrum and on surrogate surfaces. Exploratory measurements were made with a thin iron film detector for sulfuric acid droplets and a Nuclepore surrogate "leaf" for sulfur dioxide.

A preliminary recommendation was made for a practical sampling scheme capable of monitoring the major acidic gases and particles.

Phase III

This phase is the subject of the present report. The objectives include:

1. Field testing of a bubbler sampler for sulfur dioxide.
2. Direct measurements of acidic particle deposition on leaves of Ligustrum, pine needles and surrogate surfaces.
3. Further testing of a Nuclepore surrogate "leaf" as a passive sampler for sulfur dioxide which could be deployed in a plant canopy.
4. Validation of the techniques for measurement of acidic particle size distributions and additional ambient measurements.

These diverse topics have the common objective of providing measurement methods and baseline data on dry acid deposition in California.

Dry Deposition Measurements at Oildale

The Air Resources Board air monitoring station at Oildale (adjacent to Bakersfield) was selected for testing of the SO_2 bubbler, the Nuclepore passive sampler and for measurements of particle deposition on leaves and surrogate surfaces. This site was chosen because sulfur dioxide concentrations are typically among the highest in California. The site also satisfied the requirement of a minimum chance of rainfall to permit long term accumulation of particles on the leaves. The experiments were conducted from August 3 to October 18, 1984.

Bubbler Sampling of Sulfur Dioxide

Ambient concentrations of sulfur dioxide in the parts per billion range are significant for dry deposition. Electronic monitors do not have the necessary sensitivity. A bubbler containing a weak solution of hydrogen peroxide oxidizes the sulfur dioxide to sulfate which can be analyzed by ion chromatography. This is a simple sampler with high sensitivity.

The present work extends our previous experience with bubblers. Week long runs under the extremely high temperatures and low relative humidity presented a worst case test. Indeed, during the first three weeks some of the bubblers ran dry. This problem was overcome by placing a third bubbler in series with the usual two and later, by using a larger bubbler followed by a normal sized one. Aluminum foil was used as a sunshade. With these simple modifications the bubbler performed well for over two months. The sulfur dioxide concentration averaged 7.5 $\pm$ 0.3 ppb over this period.

Deposition of Particulate Sulfate and Nitrate on Leaves and Surrogate Surfaces

A direct measurement of dry deposition of acidic particles on leaves can be made by washing off the deposit and analyzing the extract. If the ambient particle concentration is measured during the exposure, deposition velocities can be derived. In previous work we have demonstrated the feasibility of this technique, using potted plants of Ligustrum. The potted plants can be transported to different sites for comparison of deposition under different conditions. The object of the present work was to measure deposition on leaves in Oildale, to investigate the effect of exposure duration on deposition velocities and to extend the technique to pine needles, since large areas of California are covered with conifers. As in the past, we also exposed plastic surrogate surfaces for comparison.

Atmospheric conditions and pollutant concentrations were remarkably constant during the first 62 days of the study. The measured deposition velocities for sulfate and nitrate were also constant for exposures ranging from 14 to 62 days. Thus the measurement technique is capable of a high degree of reproducibility. It was found that all the surfaces, natural and surrogate, collected particles at roughly the same rate. Deposits on the surrogate surfaces were confined to the top surface. Deposition velocities for sulfate were approximately 0.1 cm/sec. Nitrate deposition velocities

were 30 to 40% larger than for sulfate, attributable to the larger particle size. Deposition velocities at Oildale were generally higher than previously found at Los Angeles and Tanbark. We conclude that the leaf washing technique is useful for the study of acidic particle deposition on vegetation.

Sulfur Dioxide and Nitrogen Oxides Sampling with Nuclepore "Leaves"

Sulfur dioxide and nitrogen oxides deposit in leaves through the stomata. We have already reported some preliminary experiments with a surrogate leaf constructed of several materials in a 2 x 2 inch plastic film slide holder. The gases diffuse through the pores of the Nuclepore filter to a wet cellulose filter. The interior surfaces are extracted and analyzed by ion chromatography. The surrogate leaf is a passive sampler which can be placed in a canopy for a period limited only by the drying out time, a week or more, depending on the temperature and relative humidity. Oildale presented an extreme case of dry heat, causing filters to dry out in less than a week. This problem was solved by erecting a sunshade.

Some trials were made with smaller pore sizes and also with hydrogen peroxide solutions but these modifications were not useful. The standard version of the Nuclepore "leaf" sampled sulfate and nitrate at 10% and 8% respectively of the bubbler rate. While the Nuclepore "leaf" sampled at a consistent rate, the rate was much higher than theoretically predicted, which we tentatively ascribed to wetting of internal surfaces. Further study is required before this technique could be used for routine monitoring.

Size Distributions of Ambient Acidic Particles

The deposition velocities of acidic particles depend strongly on particle size. In preliminary work, we have shown that size distributions of individual acidic species can be measured with the Berner cascade impactor; in fact, size distributions of strong acid were obtained for the first time. To confirm and extend these results requires investigation of the general sampling characteristics of the Berner impactor as well as specific effects associated with the acidic species of interest. The necessary research has been conducted under controlled conditions using laboratory-generated aerosol and with ambient aerosol in field sampling.

The particle size-separation characteristics of the Berner impactor were measured with monodisperse (single size) laboratory aerosols. The submicron aerosol required considerable development work to produce. The Berner impactor was found to have sharp particle size separations. Measurements showed that a coating of Halocarbon grease, which is compatible with acid analysis, suppresses unwanted particle bounce in the impactor. Ammonium sulfate particles were found to be correctly sized, even at high relative humidity. Losses of ammonium nitrate from volatilization in the impactor were found to be relatively small.

Size distributions for strong acid, sulfate, nitrate, ammonium, sodium and chloride ions were obtained in Oildale and Berkeley. The data reveal interesting differences in the size distributions of individual ions and variations depending on ambient conditions. In summary, a technique has been validated for the measurement of the sizes of acidic particles, information needed for the evaluation of deposition.

Recommendations

(1) The hydrogen peroxide bubbler has been shown to be a reliable sampler for sulfur dioxide with sufficient sensitivity for dry deposition. It should be deployed in networks since the electronic monitors currently in use lack adequate sensitivity.

(2) Leaf washing yields reproducible results for nitrate and sulfate deposition. The technique has also been demonstrated for pine needles. This affords a direct measurement of deposition without the uncertainties attending other methods. Large areas of California are forested; these vulnerable targets for acid impact should be studied by the leaf washing technique.

(3) Dry deposition of acidic particles depends strongly on particle size. In this work, the Berner impactor was proven to be an excellent sampler for acidic particles; no other sampler has been so validated. Future studies of air quality in California should include particle size measurements using the techniques developed in the present work.